TIME-RESOLVED RAMAN SCATTERING IN GALLIUM NITRIDE

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We performed time-resolved anti-Stokes Raman-scattering experiments on ZnSe, GaP and hexagonal GaN in order to get information about the transient behavior of nonequilibrium phonon populations in these materials. Electrons were excited by two-photon absorption processes to exceed the large bandgaps and to provide sufficient excess energy. The relaxation of these hot electrons was measured by pump and probe experiments. From our measurements we were able to determine the LO-phonon lifetimes in all materials investigated.

In recent years the wide-bandgap semiconductor GaN has become the most promising material for optoelectronic devices working in the blue and ultraviolet (UV) spectral region[1]. The fabrication of high-brightness light-emitting devices and the very recent development of a blue laser diode[2], both based on GaN, has stimulated the rapid increase in research on GaN and its ternary alloys with InN and AlN.

GaN became interesting also for high-frequency applications and low-dimensional devices. For the development of such devices it is necessary to have information about the carrier and phonon dynamics. In high-mobility electronic devices for example it is possible to electrically excite carriers faster than the rate of energy loss to the lattice. As a result, the carriers may not be in thermal equilibrium, and it is important to understand the interaction between these hot carriers and the phonons in non-equilibrium situations. Similar issues occur in light-pumped systems or low-dimensional devices with dimensions comparable to the scattering length of the carriers in the material.

In order to get information about the interaction between hot carriers and phonons in GaN we performed time-resolved anti-Stokes Raman-scattering experiments by using pump-and-probe techniques. Our experiments reveal information about the temporal behavior of hot phonons in GaN. From the Raman signal decay we were able to determine the LO-phonon lifetimes. As expected for polar semiconductors the carrier relaxation occurs by emitting primarily longitudinal optical phonons. We compared the results obtained for GaN with similar measurements we have performed on ZnSe and GaP.

1 Experimental

The undoped (0001)-oriented GaN samples under study were grown by hydride vapor phase epitaxy on sapphire and on 6H-SiC. Their thicknesses vary between a few μm and 400 μm. The free-standing ZnSe layers and the GaP bulk crystals were grown by molecular beam epitaxy and metal organic vapor phase epitaxy, respectively.

In our measurements short laser pulses with a duration of about 4.0 ps at a repetition rate of 3.8 Mhz and energies of either 1.96 eV (632.8 nm), 2.18 eV (568 nm) or 2.41 eV (514.5nm) were generated by a cavity-dumped dye laser which was synchronously pumped by a mode-locked and frequency-doubled/tripled Nd:YAG laser. The laser beam was split into an intense pump and a less intense probe beam which were polarized

perpendicularly. Both beams were spatially recombined on the samples by passing them through an objective (x10) of a micro-Raman single-grating spectrometer equipped with a charge-coupled device (CCD) detector. The pump beam excited electron-hole pairs in the samples which were cooled down to 10 K by an Oxford microscope cryostat. Two-photon absorption made it possible to exceed the large band gap and to still provide enough excess energy to the carriers. The thus generated hot carriers thermalize to the band edge by emitting phonons which were detected through their anti-Stokes Raman signal by the less intense probe beam. The dynamics of these non-equilibrium phonons was measured by varying the delay time between pump and probe beam. Using deconvolution techniques we obtained a temporal resolution of about 0.5 ps. Because the phonons investigated have either A_1 (hexagonal GaN) or T_d (cubic ZnSe and GaP) symmetry we suppressed the disturbing background Raman signal caused by the pump beam by chosing parallel-polarized backscattering geometry.

Time-resolved anti-Stokes Raman-scattering experiments were performed first by von der Linde et al. on GaAs[3]. Due to the lack of efficient excitation sources providing enough excess energy to the carriers up to now only little was known about semiconductors with larger bandgaps like GaP (2.8eV), ZnSe (2.8eV) and GaN (3.5 eV). The technique of two-photon absorption excitation described above is an elegant method to evade UV optics.

2 Results and Discussion

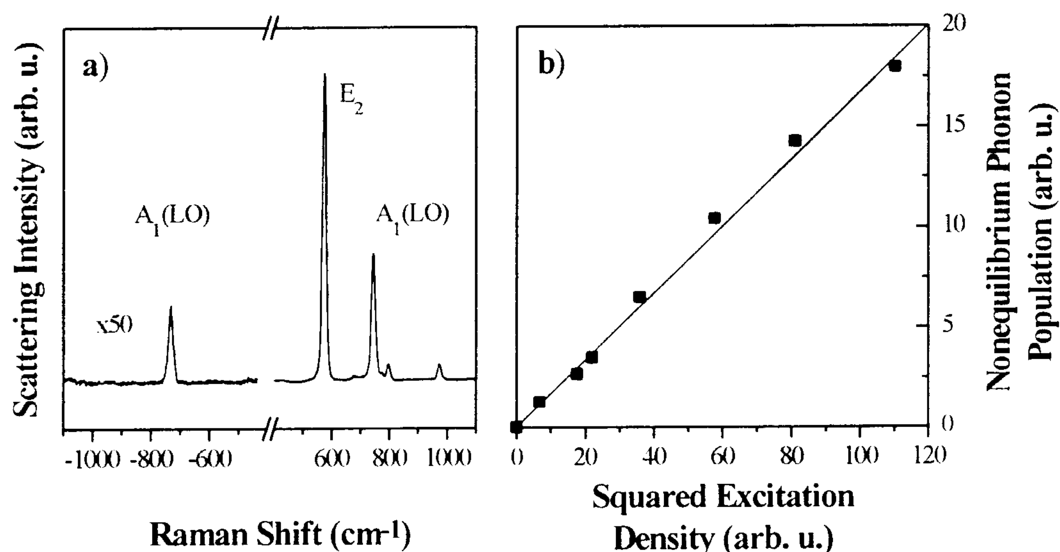

Fig. 1a: Stokes and anti-Stokes Raman spectra taken from hexagonal GaN at 10K in z(yy)z scattering geometry. For clarity, the anti-Stokes spectrum is smoothed and magnified by a factor 50.
Fig. 1b: Measured nonequilibrium phonon population as a function of the squared excitation density. The linear relationship indicates that the electron-hole pairs were generated via two-photon absorption processes.

Figure 1a) shows Stokes and anti-Stokes Raman spectra taken from hexagonal GaN at 10K in z(yy)z geometry. According to the selection rules for hexagonal GaN[4,5] the Stokes spectrum exhibits the E_2 mode located at 569cm-1 and the A_1(LO) mode at 740cm-1[5]. The other less intense modes originate from the 6H-SiC substrate. In the anti-Stokes spectrum only the A_1(LO) mode is present indicating that hot electrons were

generated and that the thermalization of these hot electrons in GaN down to the conduction-band minimum occurs by emitting primarily longitudinal optical phonons as it is expected for polar semiconductors. Considering the case of two-photon excitation of GaN by 2.41 eV laser pulses each electron could emit a maximum of 14 LO phonons. According to the Bose-Einstein distribution function[4] one can rule out that the Anti-Stokes signal is caused by thermally-activated phonons because the E_2 mode is not present in the spectrum. Assuming that the whole LO intensity would be caused by scattering from equilibrium phonons one would expect that the E_2 mode appear by a factor of 4 more in intensity than the LO mode.

Figure 1b) shows the measured nonequilibrium phonon population, i.e. the anti-Stokes Raman signal as a function of the squared excitation density. The linear relationship indicates that the electron-hole pairs were generated via two-photon absorption processes. This is an additional proof for excluding heating effects.

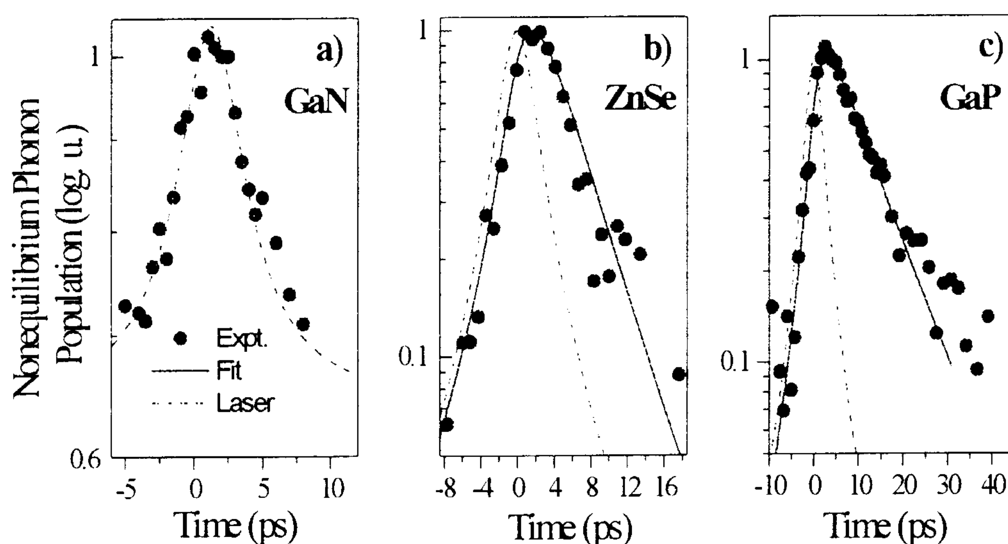

Fig. 2: Temporal behavior of the nonequilibrium phonon population in GaN (a), ZnSe (b) and GaP (c) at 10K. The lineshapes of the laser used for excitation are depicted with the dashed curves. The solid curves represent fitting transients.

Transients taken from GaP, ZnSe and GaN are depicted in Fig. 2a-c. They show the time-resolved nonequilibrium population of the LO phonons in case of the cubic semiconductors GaP and ZnSe and of the A_1(LO) phonons in case of hexagonal GaN. The autocorrelation function of the laser is indicated by the dashed curves in each figure. In order to obtain the decay time of the nonequilibrium phonon population we deconvoluted the transients with the temporal shape of the laser and assumed a monoexponential decay. Fitting the experimental data revealed for ZnSe 4.0ps and for GaP 11ps with an accuracy of 0.5ps. The value obtained for ZnSe agrees well with coherent anti-Stokes Raman-scattering experiments (CARS) performed by W. E. Bron et al.[6]. The decay time found in GaP is significantly smaller than the value known from CARS measurements. This can be explained by the two times higher excitation density used in this experiment. Since the rate for the reabsorption of hot phonons by the remaining free carriers is much higher than the decay of the hot phonons, the nonequilibrium phonon population is quenched by the

free carriers. Additionally, the carrier-carrier scattering leads to other relaxation channels than the formation of LO phonons, consequently the anti-Stokes signal loses intensity due to the lower amount of LO phonons created[7]. As can be seen in Fig. 2a the time-resolved anti-Stokes signal of GaN is almost as fast as the laser. From this we can estimate a decay time of less than 4 ps. With deconvolution techniques we obtained a decay time of 1.5 ps. CW measurements on GaN reveal a linewidth of $6cm^{-1}$. Assuming that the linewidth is broadened only homogeneously the decay time obtained is in accord with the phonon lifetime, but plasma-effects like in GaP cannot be ruled out because of the high excitation density and because of the high background doping level in our samples (higher than $1 \cdot 10^{17} cm^{-3}$).

In conclusion, we have shown results from time-resolved anti-Stokes Raman-scattering experiments on GaP, ZnSe and hexagonal GaN. Two-photon excitation was used to provide enough excess energy to the hot electrons. From the decay of the nonequilibrium phonon population we could obtain LO phonon lifetimes in the materials investigated. In order to study the influence of plasma effects on the lifetimes further measurements with a better temporal resolution and with a wider range of excitation levels are necessary.

References

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